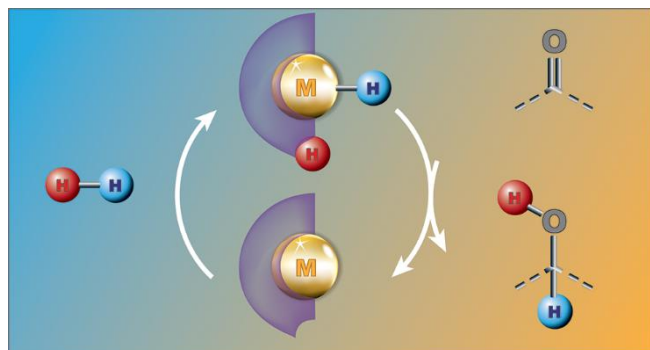


**1. Metal–Ligand Bifunctional Catalysis: the "Accepted" Mechanism, the Issue of Concertedness and the Function of the Ligand in Catalytic Cycles Involving Hydrogen Atoms**

By Dub, Pavel A.;\* Gordon, John C.

From *ACS Catalysis* (2017), 7, 6635-6655. Language: English, Database: CAPLUS, DOI:10.1021/acscatal.7b01791



For years, following the ideas of Shvo and Noyori, the core assumption of metal–ligand bifunctional mol. catalysis has relied on the direct involvement of the chelating ligand in the catalytic reaction via a reversible proton ( $H^+$ ) transfer through cleavage/formation of one of its X–H bonds ( $X = O, N, C$ ). A recently revised mechanism of the Noyori asym. hydrogenation reaction (Dub, P. A. et al. *J. Am. Chem. Soc.* **2014**, 136, 3505) suggests that the ligand is rather involved in the catalytic reaction via the stabilization of detg. transition states through N–H...O hydrogen-bonding interactions, and not via a reversible  $H^+$  transfer,...

~0 Citings

**2. Polydentate ligands and their complexes for molecular catalysis**

By Dub, Pavel A.;\* Gordon, John Cameron\*

From *U.S. Pat. Appl. Publ.* (2017), US 20170088571 A1 20170330, Language: English, Database: CAPLUS

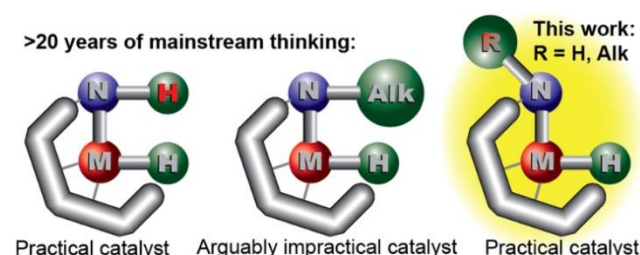
Embodiments of the present disclosure relate generally to novel achiral and chiral sulfur-, nitrogen- and phosphorus- contg. ligands, designated as NNS-type, P(O)NS-type, PNS-type, SNNS-type, SNNP(O)-type, or SNNP-type polydentate ligands and transition metal complexes of these ligands, including iridium complexes having PNS-type and NNS-type ligands. The catalysts derived from these ligands and transition metal complexes may be used in a wide range of catalytic reactions, including hydrogenation and transfer hydrogenation of unsatd. org. compds., dehydrogenation of alcs. and boranes, various...

~0 Citings

**3. Why Does Alkylation of the N–H Functionality within M/NH Bifunctional Noyori-Type Catalysts Lead to Turnover?**

By Dub, Pavel A.;\* Scott, Brian L.; Gordon, John C.\*

From *Journal of the American Chemical Society* (2017), 139(3), 1245-1260. Language: English, Database: CAPLUS, DOI:10.1021/jacs.6b11666



Mol. metal/NH bifunctional Noyori-type catalysts are remarkable in that they are among the most efficient artificial catalysts developed to date for the hydrogenation of carbonyl functionalities (loadings up to  $\sim 10^{-5}$  mol %). These catalysts typically exhibit high C=O/C=C chemo- and enantioselectivities. This unique set of properties is traditionally assocd. with the operation of an unconventional mechanism for homogeneous catalysts in which the chelating ligand plays a key role in facilitating the catalytic

reaction and enabling the aforementioned selectivities by delivering/accepting a proton ( $H^+$ ) via its N–H bond cleavage/formation. A recently revised mechanism of the Noyori hydrogenation reaction (Dub, P. A. et al. *J. Am. Chem. Soc.* **2014**, 136, 3505) suggests that the N–H bond is not cleaved but serves to stabilize the turnover-determining transition states (TDTSS) via strong N–H...O hydrogen-bonding interactions (HBIs).

~11 Citings

**PAVEL A. DUB**  
**FULL LIST OF PUBLICATIONS, PATENT APPLICATIONS AND BOOK**

**4. Macrocyclic ligands and their complexes for bifunctional molecular catalysis**

By Dub, Pavel A.;\* Schmidt, J. G.; Gordon, John C.

From [Provisional Pat. Appl. US Serial No. 62/481,427 filed on April 4, 2017](#). Language: English.

**Patent application.** The present invention relates generally to four-dentate macrocyclic ligands containing an -NH- or pyridine -(C<sub>5</sub>H<sub>3</sub>N)- functionality and transition metal complexes of these ligands, some of which are relevant to the area of metal-ligand bifunctional molecular catalysis. In particular, the catalysts can be used in a wide range of catalytic reactions, including hydrogenation and transfer hydrogenation of organic compounds containing unsaturated functionalities (C=O, C=N, C=C etc), reduction of CO<sub>2</sub>, dehydrogenation of alcohols, carboxylic acids, boranes and other compounds, various dehydrogenative couplings, C-C bond forming reactions, alkylation of amines, hydration and others

~0 Citings

**5. The mechanism of enantioselective ketone reduction with Noyori and Noyori-Ikariya bifunctional catalysts**

By Dub, Pavel A.;\* Gordon, John C.\*



From [Dalton Transactions \(2016\), 45\(16\), 6756-6781](#). Language: English, Database: CAPLUS, DOI:10.1039/C6DT00476H

A perspective (*invited review*). The catalytic hydrogenation of prochiral ketones with second and third-row transition metal complexes bearing chelating chiral ligands contg. at least one N-H functionality has achieved unparalleled performance, delivering, in the best cases, chiral alcs. with up to 99.9% ee using extremely small catalyst loadings (~10<sup>-5</sup> mol%). Hence the efficacy of this reaction has closely approached that of natural enzymic systems and the reaction itself has become one of the most efficient artificial catalytic reactions developed to date. This article describes the current level of...

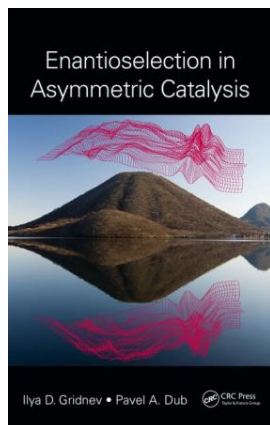
~30 Citings

**6. Enantioselection in Asymmetric Catalysis**

By Gridnev, Ilya D.; Dub, Pavel A.

From [CRC Press, Taylor & Francis Group \(2016\)](#). Language: English

ISBN 9781498726542 - CAT# K25834



A book. The field of asymmetric catalysis is currently one of the hottest areas in chemistry. This unique book focuses on the mechanism of enantioselectivity in asymmetric catalysis, rather than asymmetric catalysis from the synthetic view. It describes reliable, experimentally and computationally supported mechanisms, and discusses the danger of so-called "plausible" or "accepted" mechanisms leading to wrong conclusions. It draws parallels to enzymatic catalysis in biochemistry, and examines in detail the physico-chemical aspects of enantioselective catalysis.

~4 Citings including TCIMAIL (journal of Tokyo Chemical Industry Co., Ltd.) number 174 by T. Imamoto. Please click [here](#).

**7. First-row transition metal complexes of ENENES ligands: the ability of the thioether donor to impact the coordination chemistry**

By Dub, Pavel A.;\* Scott, Brian L.; Gordon, John C.\*

From [Dalton Transactions](#) (2016), 45(4), 1560-1571. Language: English, Database: CAPLUS, DOI:10.1039/C5DT03855C

The reactions of two variants of ENENES ligands,  $E(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{SR}$ , where E = 4-morpholinyl, R = Ph (a), Bn (b) with  $\text{MCl}_2$  (M = Mn, Fe, Co, Ni and Cu) in coordinating solvents (MeCN, EtOH) affords isolable complexes, whose magnetic susceptibility measurements suggest paramagnetism and a high-spin formulation  $[\text{MnL}^a\text{Cl}_2]$  (1),  $\text{Mn}_4\text{Cl}_2(\mu^2\text{-Cl})_4(\mu^3\text{-Cl})_2\text{L}^a_4$  (1'),  $\text{FeL}^a\text{Cl}_2$  (2),  $\text{CoLCl}_2$  (3, 4),  $\text{NiL}^b(\text{EtOH})\text{Cl}_2$ ...

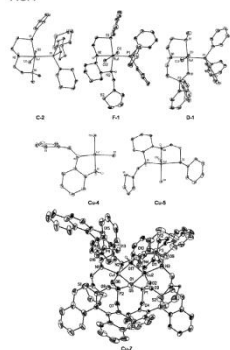
~3 Citings

**8. Preparation of polydentate ligands and their transition metal complexes for molecular catalysis**

By Dub, Pavel A.;\* Gordon, John Cameron\*

From [PCT Int. Appl.](#) (2015), [WO 2015191505 A1 20151217](#), Language: English, Database: CAPLUS

FIG. 7



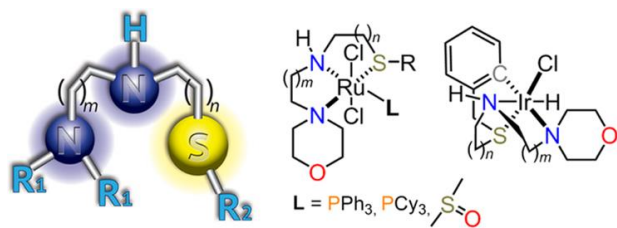
The present invention relates generally to novel achiral and chiral sulfur-, nitrogen- and phosphorus-contg. ligands (I, R<sup>1</sup>-R<sup>2</sup> = independently (un)substituted alkyl, cycloalkyl, aryl, heteroaryl, or arylalkyl; m and n = independently 1-5; q = 1-4), designated as NNS-type, P(0)NS-type, PNS-type, SNNS-type, SNNP(0)-type, or SNNP-type polydentate ligands and transition metal complexes of these ligands. The catalysts derived from these ligands and transition metal complexes may be used in a wide range of catalytic reactions, including hydrogenation and transfer hydrogenatio...

~1 Citing

**9. Air-stable NNS (ENENES) ligands and their well-defined ruthenium and iridium complexes for molecular catalysis**

By Dub, Pavel A.;\* Scott, Brian L.; Gordon, John C.\*

From [Organometallics](#) (2015), 34(18), 4464-4479. Language: English, Database: CAPLUS, DOI:10.1021/acs.organomet.5b00432



catalysts for activity and chem...

We introduce ENENES, a new family of air-stable and low-cost diamine-thioether NNS ligands bearing NH functionalities for transition metal-catalyzed chemoselective hydrogenation. Compds. I (1a-e, 2a-4a, 4b; X, X<sup>1</sup> = bond, CH<sub>2</sub>; R<sub>2</sub> = CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>, (CH<sub>2</sub>)<sub>4</sub>, Me<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>; R<sup>1</sup> = Me, Ph, PhCH<sub>2</sub>) and II (5a) and their ruthenium and iridium complexes were prepd.; the complexes were examd. as

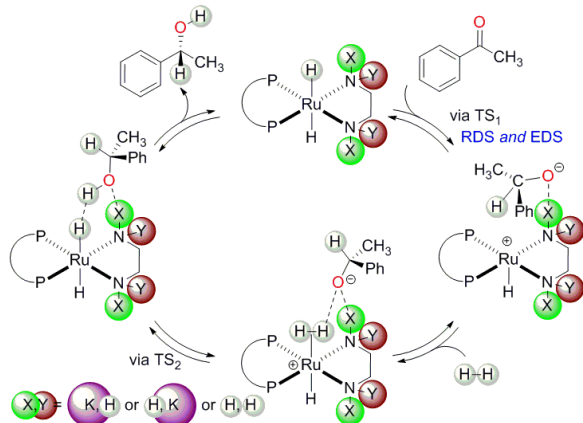
~9 Citings

**10. Unravelling the Mechanism of the Asymmetric Hydrogenation of Acetophenone by [RuX<sub>2</sub>(diphosphine)(1,2-diamine)] Catalysts**

By Dub, Pavel A.;\* Henson, Neil J.; Martin, Richard L.; Gordon, John C.\*

From [Journal of the American Chemical Society](#) (2014), 136(9), 3505-3521. Language: English, Database:

CAPLUS, DOI:10.1021/ja411374j



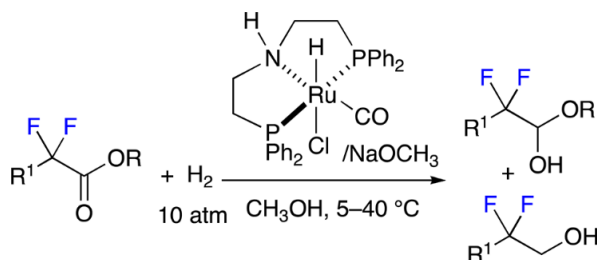
The mechanism of catalytic hydrogenation of acetophenone by the chiral complex *trans*-[RuCl<sub>2</sub>{(S)-binap}{(S,S)-dppe}] and KO<sup>t</sup>-C<sub>4</sub>H<sub>9</sub> in propan-2-ol is revised on the basis of DFT computations carried out in dielec. continuum and the most recent exptl. observations. The results of these collective studies suggest that neither a six-membered pericyclic transition state nor any multibond concerted transition states are involved. Instead, a hydride moiety is transferred in an outer-sphere manner to afford an ion-pair, and the corresponding transition state is both ...

~60 Citings

### 11. Practical Selective Hydrogenation of $\alpha$ -Fluorinated Esters with Bifunctional Pincer-Type Ruthenium(II) Catalysts Leading to Fluorinated Alcohols or Fluoral Hemiacetals

By Otsuka, Takashi; Ishii, Akihiro; Dub, Pavel A.; Ikariya, Takao

From *Journal of the American Chemical Society* (2013), 135(26), 9600-9603. Language: English, Database: CAPLUS, DOI:10.1021/ja403852e



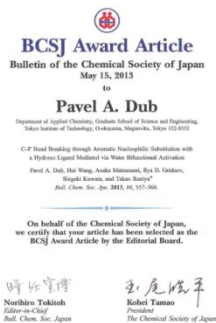
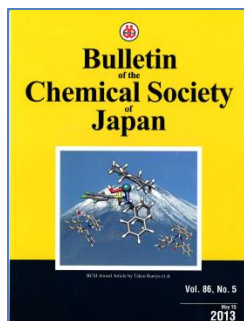
Selective hydrogenation of fluorinated esters with pincer-type bifunctional catalysts RuHCl(CO)(dpa) 1a, *trans*-RuH<sub>2</sub>(CO)(dpa) 1b, and *trans*-RuCl<sub>2</sub>(CO)(dpa) 1c (I; X = H, Cl; H, H; Cl, Cl, resp.) under mild conditions proceeds rapidly to give the corresponding fluorinated alcs. or hemiacetals in good to excellent yields. Under the optimized conditions, the hydrogenation of chiral (*R*)-2-fluoropropionate proceeds smoothly to give the corresponding chiral alc. without any serious decrease of the ee value.

~43 Citings

### 12. C-F Bond Breaking through Aromatic Nucleophilic Substitution with a Hydroxo Ligand Mediated via Water Bifunctional Activation

By Dub, Pavel A.; Wang, Hui; Matsunami, Asuka; Gridnev, Ilya D.; Kuwata, Shigeki; Ikariya, Takao

From *Bulletin of the Chemical Society of Japan* (2013), 86(5), 557-568. Language: English, Database: CAPLUS, DOI:10.1246/bcsj.20120359; *Bulletin of the Chemical Society of Japan Award Article*, May 2013



Transformation of C-F to C-O bond mediated by bifunctional Ru and Ir complexes is described. This reaction proceeds through water O-H bond cleavage via metal-ligand cooperation in the newly developed 16e bifunctional Ru and Ir complexes bearing chiral (S,S)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>-dppe ligand. The 16e Ru amido complex, [Ru{(S,S)-Pfbdsdppe}(η<sup>6</sup>-hmb)] (1a), readily reacted with H<sub>2</sub>O at room temp. producing oxometallacyclic compd., (*R*)-[Ru{κ<sup>3</sup>(N,N',O)-(S,S)-OC<sub>6</sub>F<sub>4</sub>SO<sub>2</sub>dppe}(η<sup>6</sup>-hmb)] (3aR), as a re...

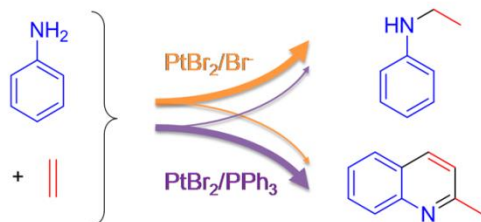
~10 Citings



### 13. Platinum-catalyzed assembly of quinaldine from aniline and ethylene

By Bethegnies, Aurelien; Dub, Pavel A.; Poli, Rinaldo

From *Organometallics* (2013), 32(6), 1882-1891. Language: English, Database: CAPLUS, DOI:10.1021/om400020k



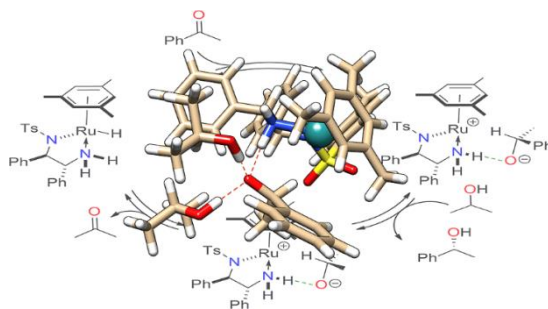
The selectivity of the catalytic reaction between aniline and ethylene in the presence of the Brunet catalyst ( $\text{PtBr}_2/\text{Br}^-$ ) shifts from the hydroamination product N-ethylaniline to the heterocyclization product 2-methylquinoline (quinaldine) when conducted in the presence of  $\text{PPh}_3$  (1 equiv per Pt atom). Condition optimization revealed that this process works best in the absence of any halide salt additive, that it is essentially insensitive to the nature of the halide in  $\text{PtX}_2$ , that the best promoter in the  $\text{PMexPh}_{3-x}$  series is  $\text{PPh}_3$ .

~3 Citings

### 14. Quantum Chemical Calculations with the Inclusion of Nonspecific and Specific Solvation: Asymmetric Transfer Hydrogenation with Bifunctional Ruthenium Catalysts

By Dub, Pavel A.; Ikariya, Takao

From *Journal of the American Chemical Society* (2013), 135(7), 2604-2619. Language: English, Database: CAPLUS, DOI:10.1021/ja3097674



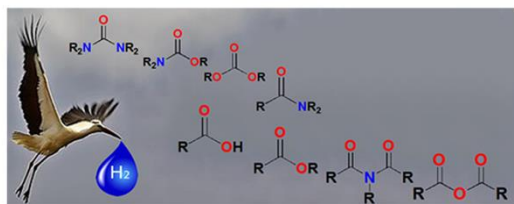
Details of the mechanism of asym. transfer hydrogenation of ketones catalyzed by two chiral bifunctional ruthenium complexes, (S)- $\text{RuH}[(R,R)\text{-OCH(Ph)CH(Ph)NH}_2](\eta^6\text{-benzene})$  (Ru-1) or (S)- $\text{RuH}[(R,R)\text{-p-TsNCH(Ph)CH(Ph)NH}_2](\eta^6\text{-mesitylene})$  (Ru-2), were studied computationally by d. functional theory, accounting for the solvation effects by using continuum, discrete, and mixed continuum/discrete solvation models via "solvated supermols." approach. In contrast to gas phase quantum chem. calcns., where the reactions were found to proceed via a concerted three-...

~75 Citings

### 15. Catalytic Reductive Transformations of Carboxylic and Carbonic Acid Derivatives Using Molecular Hydrogen

By Dub, Pavel A.; Ikariya, Takao

From *ACS Catalysis* (2012), 2(8), 1718-1741. Language: English, Database: CAPLUS, DOI:10.1021/cs300341g



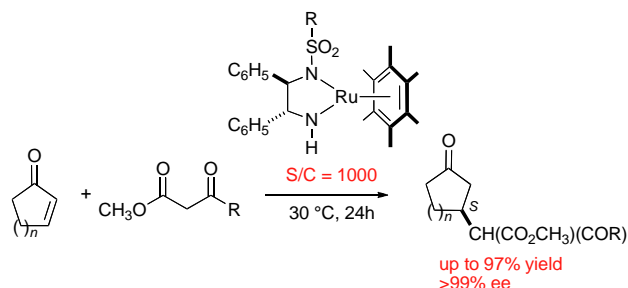
A review (*invited*). A comprehensive overview on homogeneous catalytic hydrogenation of carboxylic acids and its derivs. as well as carbonic acid derivs. with transition metal-based mol. catalysts is described. Despite the tremendous potential in the hydrogenation of these less electrophilic carbonyl compds. using mol. hydrogen in synthetic org. chem., their redn. still relies mostly on the stoichiometric use of metal hydride reagents, such as  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ , and their

derivs. For the past decade, a significant and rapid progress in particularly ester hydrogenation has been achie...

~119 Citings

## 16. A practical asymmetric conjugate addition to cyclic enones with chiral bifunctional Ru amido catalysts

By Dub, Pavel A.; Wang, Hui; Watanabe, Masahito; Gridnev, Ilya D.; Ikariya, Takao  
From *Tetrahedron Letters* (2012), 53(27), 3452-3455. Language: English, Database: CAPLUS, DOI:10.1016/j.tetlet.2012.04.100



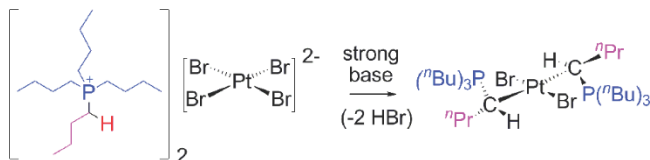
A practical asym. C-C bond formation to synthetically useful  $\beta$ -chiral cyclic ketones (>99% ee) using bifunctional chiral amido Ru catalysts under an S/C = 1000, the highest ratio achieved so far in the literature for this class of reactions, is described. The catalytic reactivity decreases in the order of Ru(Msdpen)(hmb) > Ru(Pfbsdpen)(hmb) > Ru(Tsdpen)(hmb) > Ru(PMsdpn)(hmb), where Ru(Pfbsdpen)(hmb) is a newly developed chiral bifunctional catalyst. Complex Ru(Msdpen)(hmb) was identified as the best in terms of reactivity and enantioface selectivity, whereas Ru(PMsdpn)(hmb) g...

~15 Citings

The reaction is highlighted in Synfacts 2012 (H. Yamamoto). Please click [here](#).

## 17. Formation and Structure of a Platinum(II) Complex Containing Two trans Nonstabilized Phosphorus Ylide Ligands: Evidence for Reversible Ylide Dissociation

By Dub, Pavel A.; Bethegnies, Aurelien; Daran, Jean-Claude; Poli, Rinaldo  
From *Organometallics* (2012), 31(8), 3081-3086. Language: English, Database: CAPLUS, DOI:10.1021/om2012453

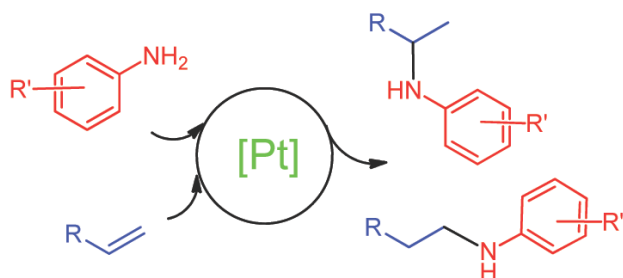


The reaction of (Bu<sub>4</sub>P)<sub>2</sub>[PtBr<sub>4</sub>] with 2,2'-(C<sub>6</sub>H<sub>4</sub>Li)<sub>2</sub> yields selectively (by <sup>195</sup>Pt and <sup>31</sup>P NMR) *trans*-PtBr<sub>2</sub>[CHPr(PBu<sub>3</sub>)<sub>2</sub>]<sub>2</sub> as a mixt. of meso(*R,S*) and dl(*R,R* + *S,S*) diastereoisomers. The initially formed 1:1 mixt. slowly evolves toward a soln. richer in the meso compd., which then crystallizes selectively. In addn. to the NMR characterization, the meso isomer also was characterized by a single-crystal x-ray diffraction anal. DFT calcns. in the gas phase and in soln. (THF) con...

~3 Citings

## 18. DFT and experimental studies on the PtX<sub>2</sub>/X<sup>-</sup>-catalyzed olefin hydroamination: effect of halogen, amine basicity, and olefin on activity, regioselectivity, and catalyst deactivation

By Dub, Pavel A.; Bethegnies, Aurelien; Poli, Rinaldo  
From *Organometallics* (2012), 31(1), 294-305. Language: English, Database: CAPLUS, DOI:10.1021/om2009149



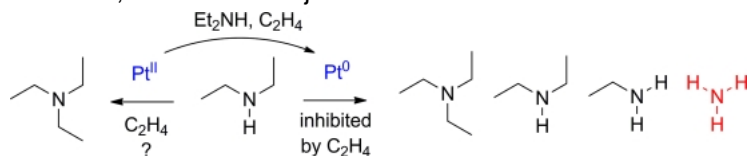
Mechanism of hydroamination of ethylene with aniline, catalyzed by platinum halide system, PtX<sub>2</sub>/X<sup>-</sup> was investigated by DFT calcns. of potential energy surface of insertion-oxidative addn.-reductive elimination pathway. A DFT/B3LYP study with inclusion of solvent and temp. effects has probed the olefin activation mechanism for the intermol. hydroamination of ethylene and 1-hexene by aniline derivs. catalyzed by the PtX<sub>2</sub>/X<sup>-</sup> system on the basis of a variety of exptl. results, including new expts. on catalyst deactivation. For ethylene and aniline, th...

~15 Citings

## 19. Reactions of diethylamine and ethylene catalyzed by Pt<sup>II</sup> or Pt<sup>0</sup> - Transalkylation vs. Hydroamination

By Dub, Pavel A.; Bethegnies, Aurelien; Poli, Rinaldo

From *European Journal of Inorganic Chemistry* (2011), 2011(33), 5167-5172. Language: English, Database: CAPLUS, DOI:10.1002/ejic.201100624



PtBr<sub>2</sub>/nBu<sub>4</sub>PBr (without solvent) or K<sub>2</sub>PtCl<sub>4</sub>/NaBr (in water) have been shown to efficiently catalyze the hydroamination of ethylene by aniline and are poor catalysts for the hydroamination of ethylene by diethylamine. A DFT study on the hydroamination

mechanism indicates that the energetic span of the C<sub>2</sub>H<sub>4</sub>/Et<sub>2</sub>NH catalytic cycle is close to that of the C<sub>2</sub>H<sub>4</sub>/PhNH<sub>2</sub> cycle. The poor performance is attributed to rapid catalyst degradn. with redn. to metallic platinum. Pt<sup>0</sup>, on the...

~7 Citings

## 20. Modeling the platinum-catalyzed intermolecular hydroamination of ethylene: The nucleophilic addition of HNEt<sub>2</sub> to coordinated ethylene in *trans*-PtBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(HNEt<sub>2</sub>)

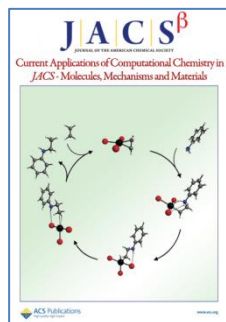
By Dub, Pavel A.; Daran, Jean-Claude; Levina, Vladislava A.; Belkova, Natalia V.; Shubina, Elena S.; Poli, Rinaldo  
From *Journal of Organometallic Chemistry* (2011), 696(6), 1174-1183. Language: English, Database: CAPLUS, DOI:10.1016/j.jorganchem.2010.09.043

Compd. *trans*-PtBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(HNEt<sub>2</sub>) (1) has been synthesized by Et<sub>2</sub>NH addn. to K[PtBr<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)] and structurally characterized. Its isomer *cis*-PtBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(HNEt<sub>2</sub>) (3) has been obtained from 1 by photolytic dissociation of ethylene, generating the dinuclear *trans*-[PtBr<sub>2</sub>(HNEt<sub>2</sub>)]<sub>2</sub> intermediate (2), followed by thermal re-addn. of C<sub>2</sub>H<sub>4</sub>, but only in low yields. The addn. of further Et<sub>2</sub>NH to 1 in either dichloromethane...

~14 Citings

## 21. The Pt-catalyzed ethylene hydroamination by aniline: a computational investigation of the catalytic cycle

By Dub, Pavel A.; Poli, Rinaldo



From *Journal of the American Chemical Society* (2010), 132(39), 13799-13812. Language: English, Database: CAPLUS, DOI:10.1021/ja1051654; *JACS Select* # 13, Ed. Prof. Weston T. Borden (2011) "Current Applications of Computational Chemistry in JACS – Molecules, Mechanisms and Materials".

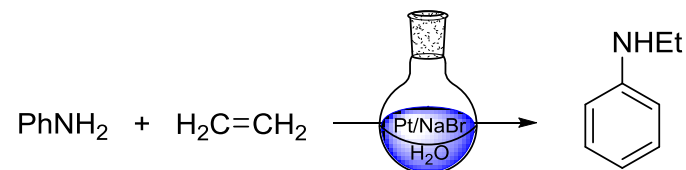
A full QM DFT study without system simplification and with the inclusion of solvation effects in aniline as solvent has addressed the addn. of aniline to ethylene catalyzed by PtBr<sub>2</sub>/Br<sup>-</sup>. The resting state of the catalytic cycle is the [PtBr<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)]<sup>-</sup> complex (2). A cycle involving aniline activation by N-H oxidative addn. was found energetically prohibitive. The operating cycle involves ethylene activation followed by nucleophilic addn. of aniline to the coordinated ethylene, intramol. transfer of the ammonium proton to the m...

~38 Citings

## 22. Hydroamination of ethylene by aniline: catalysis in water

By Dub, Pavel A.; Rodriguez-Zubiri, Mireia; Baudequin, Christine; Poli, Rinaldo

From *Green Chemistry* (2010), 12(8), 1392-1396. Language: English, Database: CAPLUS, DOI:10.1039/c004727a



The platinum-catalyzed and halide-promoted hydroamination of ethylene with aniline is reported for the first time in the presence of simple sodium halides in water. Compds. K<sub>2</sub>PtX<sub>4</sub> (X = Cl or Br), PtX<sub>2</sub> or PtX<sub>4</sub> (0.3% mol) in the presence of an aq. soln. of excess NaX and aniline under ethylene pressure (25 bar) affords N-

ethylaniline with 60-85 turnovers after 10 h at 150 °C. The best result (TON = 85) was obtained in the presence of excess NaBr, whereas a slightly lower activity was obsd. with NaCl (60 cycles) and practically no activity with NaF o...

~23 Citings

**23. A computational study of solution equilibria of platinum-based ethylene hydroamination catalytic species including solvation and counterion effects: Proper treatment of the free energy of solvation**

By Dub, Pavel A.; Poli, Rinaldo

From *Journal of Molecular Catalysis A: Chemical* (2010), 324(1-2), 89-96. Language: English, Database: CAPLUS, DOI:10.1016/j.molcata.2010.03.003

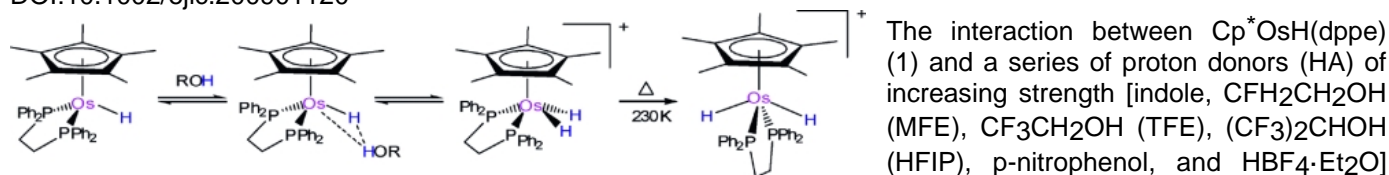
A DFT/B3LYP study of the effect of the explicit inclusion of the Me<sub>4</sub>P<sup>+</sup> cation (as a model of nBu<sub>4</sub>P<sup>+</sup>) on the calcn. of soln. equil. involving anionic Pt<sup>II</sup> complexes is reported. The calcd. complexes are models of species that potentially participate in the low-energy portion of the catalytic cycle of the ethylene hydroamination by aniline catalyzed by the PtBr<sub>2</sub>/(nBu<sub>4</sub>P)Br system, namely (nBu<sub>4</sub>P)<sub>2</sub>[PtBr<sub>4</sub>] (1), (nBu<sub>4</sub>P)<sub>2</sub>[Pt<sub>2</sub>Br<sub>6</sub>] (1'), (nBu<sub>4</sub>P)<sub>2</sub>[PtBr<sub>6</sub>]<sup>-</sup> (1'').

**~30 Citings**

## 24. Protonation of Cp\**M*(dppe)H Hydrides: Peculiarities of the Osmium Congener

By Dub, Pavel A.; Fillipov, Oleg A.; Silantyev, Gleb A.; Belkova, Natalia V.; Daran, Jean-Claude; Epstein, Lina M.; Poli, Rinaldo; Shubina, Elena S.

From [European Journal of Inorganic Chemistry](#) (2010), (10), 1489-1500. Language: English, Database: CAPLUS, DOI:10.1002/ejic.200901120



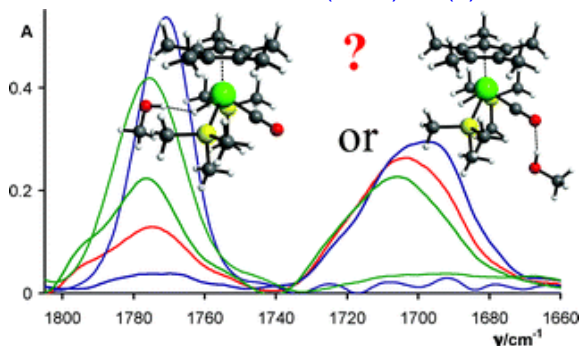
has been investigated exptl. by variable temp. IR and NMR spectroscopy in solvents with different coordinating abilities (alkanes, dichloromethane and their mixts.) and computationally at the DFT/B3PW91 level using different models. Both the IR and NMR spectroscopic data for the interaction with weak proton ...

**~10 Citings**

## 25. Hydrogen bonding to carbonyl hydride complex $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ and its role in proton transfer

By Dub, Pavel A.; Filippov, Oleg A.; Belkova, Natalia V.; Daran, Jean-Claude; Epstein, Lina M.; Poli, Rinaldo; Shubina, Elena S.

From [Dalton Transactions \(2010\)](#), 39(8), 2008-2015. Language: English, Database: CAPLUS, DOI:10.1039/b916084a



The interaction of the carbonyl hydride complex  $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$  with Bronsted (fluorinated alcs.,  $(\text{CF}_3)_n\text{CH}_3\text{-nOH}$  ( $n = 1\text{-}3$ ), and  $\text{CF}_3\text{COOH}$ ) and Lewis ( $\text{Hg}(\text{C}_6\text{F}_5)_2$ ,  $\text{BF}_3\cdot\text{OEt}_2$ ) acids was studied by variable temp. IR and NMR ( $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$ ) spectroscopies in combination with DFT/B3LYP calcns. Among the two functionalities potentially capable of the interaction - carbonyl and hydride ligands - the first was found to be the preferential bin...

**~14 Citings**

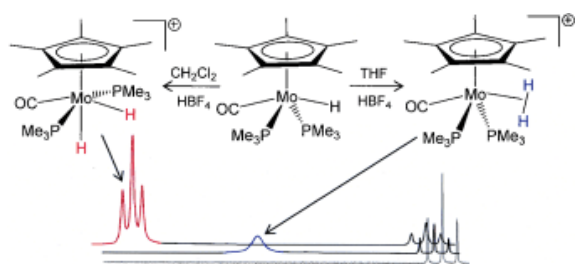
**26. Solvent-Dependent Dihydrogen/Dihydride Stability for  $[\text{Mo}(\text{CO})(\text{Cp}^*)\text{H}_2(\text{PMe}_3)_2]^+[\text{BF}_4]^-$  Determined by Multiple Solvent...Anion...Cation Non-Covalent Interactions**

By Dub, Pavel A.; Belkova, Natalia V.; Filippov, Oleg A.; Daran, Jean-Claude; Epstein, Lina M.; Lledós, Agustí; Shubina, Elena S.; Poli, Rinaldo

From [Chemistry - A European Journal](#) (2010), 16(1), 189-201, S189/1-S189/35. Language: English, Database:



CAPLUS, DOI:10.1002/chem.200901613



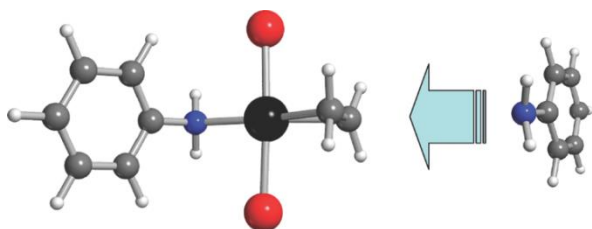
Low-temp. (200 K) protonation of  $[\text{Mo}(\text{CO})(\text{Cp}^*)\text{H}(\text{PMe}_3)_2]$  (1) by  $\text{Et}_2\text{O} \cdot \text{HBF}_4$  gives a different result depending on a subtle solvent change: The dihydrogen complex  $[\text{Mo}(\text{CO})(\text{Cp}^*)(\eta^2\text{-H}_2)(\text{PMe}_3)_2]^+$  (2) is obtained in THF, whereas the tautomeric classical dihydride  $[\text{Mo}(\text{CO})(\text{Cp}^*)(\text{H})_2(\text{PMe}_3)_2]^+$  (3) is the only observable product in dichloromethane. Both products were fully characterized (vCO IR;  $^1\text{H}$ ,  $^{31}\text{P}$ ...

~26 Citings

## 27. Platinum-Catalyzed Ethylene Hydroamination with Aniline: Synthesis, Characterization, and Studies of Intermediates

By Dub, Pavel A.; Rodriguez-Zubiri, Mireia; Daran, Jean-Claude; Brunet, Jean-Jacques; Poli, Rinaldo

From *Organometallics* (2009), 28(16), 4764-4777. Language: English, Database: CAPLUS, DOI:10.1021/om9002494



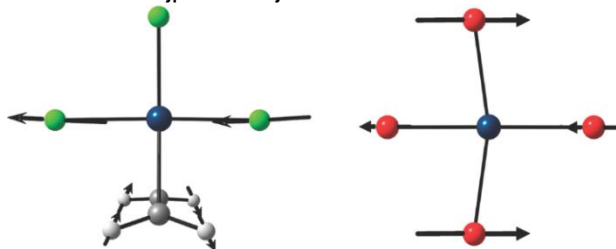
Starting from either  $\text{K}_2\text{PtCl}_4$  or  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$  (Zeise's salt), complexes  $(\text{Bu}_4\text{P})_2[\text{PtBr}_4]$  (1),  $\text{Bu}_4\text{P}[\text{PtBr}_3(\text{C}_2\text{H}_4)]$  (2),  $\text{Bu}_4\text{P}[\text{PtBr}_3(\text{PhNH}_2)]$  (3), *trans*- $[\text{PtBr}_2(\text{C}_2\text{H}_4)(\text{PhNH}_2)]$  (4), *cis*- $[\text{PtBr}_2(\text{C}_2\text{H}_4)(\text{PhNH}_2)]$  (5), and *cis*- $[\text{PtBr}_2(\text{PhNH}_2)_2]$  (6) were obtained by efficient 1-pot procedures. All were fully charact...

~42 Citings

## 28. Experimental (IR, Raman) and Computational Analysis of a Series of $\text{PtBr}_2$ Derivatives: Vibrational Coupling in the Coordinated Ethylene and Pt-Br Modes

By Dub, Pavel A.; Filippov, Oleg A.; Belkova, Natalia V.; Rodriguez-Zubiri, Mireia; Poli, Rinaldo

From *Journal of Physical Chemistry A* (2009), 113(22), 6348-6355. Language: English, Database: CAPLUS, DOI:10.1021/jp902394j



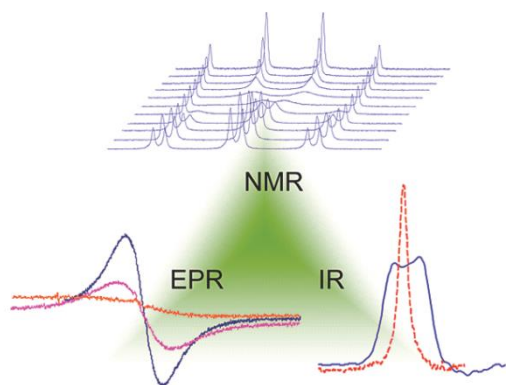
$(\text{nBu}_4\text{P})[\text{PtBr}_3(\text{C}_2\text{H}_4)]$  (1), *trans*- $[\text{PtBr}_2(\text{NH}_2\text{Ph})(\text{C}_2\text{H}_4)]$  (2), *cis*- $[\text{PtBr}_2(\text{NH}_2\text{Ph})(\text{C}_2\text{H}_4)]$  (3),  $(\text{nBu}_4\text{P})_2[\text{PtBr}_4]$  (4),  $(\text{nBu}_4\text{P})[\text{PtBr}_3(\text{NH}_2\text{Ph})]$  (5), and *cis*- $[\text{PtBr}_2(\text{NH}_2\text{Ph})_2]$  (6), as well as the trichloro analog of 1,  $(\text{nBu}_4\text{P})[\text{PtCl}_3(\text{C}_2\text{H}_4)]$  (1Cl), were studied exptl. by both IR and Ram...

~9 Citings

## 29. Investigation of the $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}]^{n+}$ ( $n = 0, 1$ ) Redox Pair: Dynamic Processes on Very Different Time Scales

By Baya, Miguel; Dub, Pavel A.; Houghton, Jennifer; Daran, Jean-Claude; Belkova, Natalia V.; Shubina, Elena S.; Epstein, Lina M.; Lledós, Agustí; Poli, Rinaldo

From *Inorganic Chemistry* (2009), 48(1), 209-220. Language: English, Database: CAPLUS, DOI:10.1021/ic801676n



The compd.  $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}]$  (1) is reversibly oxidized at  $E_{1/2} = -1.40$  V vs. ferrocene in MeCN. Its oxidn. with  $\text{Cp}_2\text{FePF}_6$  yields thermally stable  $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}]\text{PF}_6$  (2), which has been isolated and characterized by IR and EPR spectroscopy and by single-crystal x-ray diffraction. The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of 1 show two types of  $\text{PMe}_3$  ligands in a 1:2 ratio at low temp., but only one av. signal at room temp., with activation parameters of  $\Delta H \dots$

~14 Citings

### 30. Effect of the nature of the metal atom on hydrogen bonding and proton transfer to $[\text{Cp}^*\text{MH}_3(\text{dppe})]$ : tungsten versus molybdenum

By Belkova, Natalia V.; Besora, Maria; Baya, Miguel; Dub, Pavel A.; Epstein, Lina M.; Lledós, Agustí; Poli, Rinaldo; Revin, Pavel O.; Shubina, Elena S.

From [Chemistry - A European Journal](#) (2008), 14(32), 9921-9934. Language: English, Database: CAPLUS, DOI:10.1002/chem.200801003

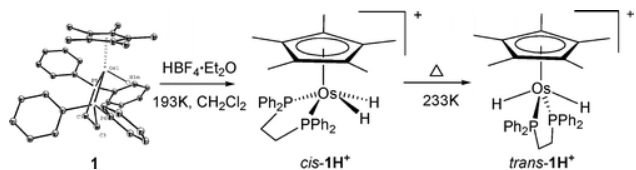
The hydrogen-bonding and proton-transfer pathway to complex  $[\text{Cp}^*\text{W}(\text{dppe})\text{H}_3]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) was investigated exptl. by IR, NMR, UV-vis. spectroscopy in the presence of fluorinated alcs., *p*-nitrophenol, and  $\text{HBF}_4$ , and by using DFT calcns. for the  $[\text{CpW}(\text{dhpe})\text{H}_3]$  model ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ;  $\text{dhpe} = \text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2$ ) and for the real system. A study of the interaction with weak aci...

~23 Citings

### 31. Synthesis and Protonation Studies of $\text{Cp}^*\text{Os}(\text{dppe})\text{H}$ : Kinetic versus Thermodynamic Control

By Dub, Pavel A.; Belkova, Natalia V.; Lyssenko, Konstantin A.; Silantyev, Gleb A.; Epstein, Lina M.; Shubina, Elena S.; Daran, Jean-Claude; Poli, Rinaldo

From [Organometallics](#) (2008), 27(13), 3307-3311. Language: English, Database: CAPLUS, DOI:10.1021/om8000235



The previously undescribed complex  $\text{Cp}^*\text{Os}(\text{dppe})\text{H}$  (1) was synthesized starting from either  $\text{K}_2\text{OsX}_6$  salts or  $\text{H}_2\text{OsBr}_6$  and characterized together with its precursors  $\text{Cp}^*\text{Os}(\text{COD})\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ). Protonation of 1 by  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  was studied in  $\text{CD}_2\text{Cl}_2$  at 193 K and was found to lead exclusively to *cis*- $[\text{Cp}^*\text{Os}(\text{dppe})(\text{H})_2]^+\text{BF}_4^-$ , which irreversibly transforms into *trans*- $[\text{Cp}^*\text{Os}(\text{dppe})(\text{H})_2]^+\text{BF}_4^- \dots$

~13 Citings

### 32. Solvent control in the protonation of $[\text{Cp}^*\text{Mo}(\text{dppe})\text{H}_3]$ by $\text{CF}_3\text{COOH}$

By Dub, Pavel A.; Baya, Miguel; Houghton, Jennifer; Belkova, Natalia V.; Daran, Jean-Claude; Poli, Rinaldo; Epstein, Lina M.; Shubina, Elena S.

From [European Journal of Inorganic Chemistry](#) (2007), (18), 2813-2826. Language: English, Database: CAPLUS,

DOI:10.1002/ejic.200700021; *Special 10<sup>th</sup> anniversary issue (invited)*.

The outcome of the reaction between [Cp\*Mo(dppe)H<sub>3</sub>] [dppe = 1,2-bis(diphenylphosphino)ethane] and trifluoroacetic acid (TFA) is highly dependent on the solvent and the TFA/Mo ratio. The dihydride compd. [Cp\*Mo(dppe)H<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)] is formed selectively when the reaction is carried out in arom. hydrocarbons (benzene, toluene) when using less than one equiv of TFA. The dihydride is also the end product when THF or MeCN are used as solvent, independent of the TFA/Mo ratio. In benzene/toluene the use of excess acid has a profound ef...

~21 Citings

### 33. Kinetics and thermodynamics of proton transfer to Cp\*Ru(dppe)H: Via dihydrogen bonding and (η<sup>2</sup>-H<sub>2</sub>)-complex to the dihydride

By Belkova, Natalia V.; Dub, Pavel A.; Baya, Miguel; Houghton, Jennifer

From *Inorganica Chimica Acta* (2007), 360(1), 149-162. Language: English, Database: CAPLUS, DOI:10.1016/j.ica.2006.07.106; *Special issue "Inorganic Chemistry – The Next Generation"*.

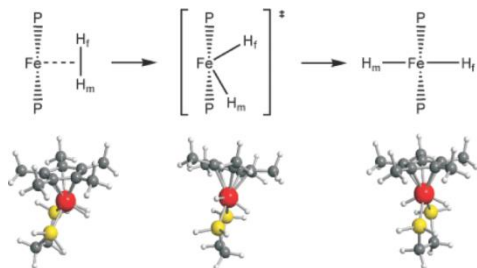
The interaction between Cp\*RuH(dppe) and proton donors (HA) of increasing strength: CFH<sub>2</sub>CH<sub>2</sub>OH (MFE), CF<sub>3</sub>CH<sub>2</sub>OH (TFE), (CF<sub>3</sub>)<sub>2</sub>CHOH (HFIP), *p*-nitrophenol, CF<sub>3</sub>COOH and HBF<sub>4</sub> were studied spectroscopically by variable-temp. IR, UV-visible, and NMR spectroscopy in solvents of differing polarity (*n*-hexane, CH<sub>2</sub>Cl<sub>2</sub> and their mixt.). The low-temp. IR study shows the establishment of a H bond which involves the hydride ligand as the proton accepting site. The basicity factor E<sub>j</sub> < /...

~36 Citings

### 34. Dihydrogen to Dihydride Isomerization Mechanism in [(C<sub>5</sub>Me<sub>5</sub>)FeH<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)]<sup>+</sup> through the Experimental and Theoretical Analysis of Kinetic Isotope Effects

By Baya, Miguel; Maresca, Olivier; Poli, Rinaldo; Coppel, Yannick; Maseras, Feliu; Lledós, Agustí; Belkova, Natalia V.; Dub, Pavel A.; Epstein, Lina M.; Shubina, Elena S.

From *Inorganic Chemistry* (2006), 45(25), 10248-10262. Language: English, Database: CAPLUS, DOI:10.1021/ic061428n



The isomerization of [Cp\*Fe(dppe)(η<sup>2</sup>-H<sub>2</sub>)]<sup>+</sup>, generated in situ by low-temp. protonation of Cp\*Fe(dppe)H with either HBF<sub>4</sub> or CF<sub>3</sub>COOH, to the dihydride tautomer trans-[Cp\*Fe(dppe)(H)<sub>2</sub>]<sup>+</sup> is irreversible and follows 1st-order kinetics in the -10 to +15° range with ΔH = 21.6 ± 0.8 kcal mol<sup>-1</sup> and ΔS = 5 ± 3 eu. The isomerization rate const. is essentially independent of the nature and quantity of a strong acid. D. functional theory (DFT) calcns. on variou...

~27 Citings

### 35. Experimental and computational studies of hydrogen bonding and proton transfer to [Cp\*Fe(dppe)H]

By Belkova, Natalia V.; Collange, Edmond; Dub, Pavel; Epstein, Lina M.; Lemenovskii, Dmitrii A.; Lledós, Agustí; Maresca, Olivier; Maseras, Feliu; Poli, Rinaldo; Revin, Pavel O.; et al

From *Chemistry - A European Journal* (2005), 11(3), 873-888. Language: English, Database: CAPLUS, DOI:10.1002/chem.200400700

This article reports exptl. and computational studies of the interaction between [Cp\*Fe(dppe)H] and different proton donors (HA). The focus is on the structure of the proton transfer intermediates and on the potential energy surface of the proton transfer leading to the dihydrogen complex [Cp\*Fe(dppe)(H<sub>2</sub>)]<sup>+</sup>. With *p*-nitrophenol (PNP) a UV/Visible study provides evidence of the formation of the ion pair stabilized by a hydrogen bond between the nonclassical cation [Cp\*Fe(dppe)(H<sub>2</sub>)]<sup>+</sup> and the homo conjugated anion ([AH...]

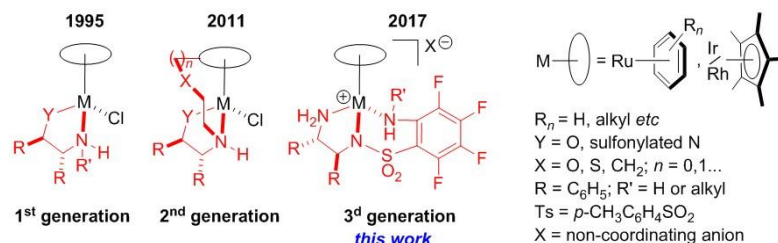
~55 Citings

**Summary:** >754 citations; h-index = 15 (accessed on August 2017; Google Scholar). All the citations are based on the Google Scholar, Scifinder or Crossref (August 2017). The following papers are in preparation (drafts are available on demand). Corresponding author highlighted by \*.

### 36. Synthetic Journey Towards the Third Generation of the Noyori-Ikariya (Pre)catalysts

By Dub, Pavel A.;\* Matsunami, Asuka; Kuwata, Shigeki; Kayaki, Yoshihito\*

For the submission to [Journal of the American Chemical Society \(2017-18\)](#).



The Noyori-Ikariya asymmetric transfer hydrogenation (ATH) reaction represents one of the largest-volume applications of bifunctional catalysts in fine chemical industry. The method allows for the preparation of chiral secondary alcohols or amines with very good to excellent optical purities (96–99% ee). This paper describes syntheses, characterizations and synthetic journey

towards the 3<sup>d</sup> ionic generation of Noyori-Ikariya molecular (pre)catalysts. The work presented here started out of from the project aiming to investigate the possibility to cleave N–H bond of ammonia via metal–ligand cooperation based on the platform of the 1<sup>st</sup> generation of such complexes. For example, 16e<sup>−</sup> chiral amido complexes [Ru{(S,S)-TsDPEN}(η<sup>6</sup>-p-cymene)] **1**, [Ru{(S,S)-TfDPEN}(η<sup>6</sup>-hmb)] **2** and [Cp\*Ir{(S,S)-TfDPEN}] **3** react reversibly with ammonia in dichloromethane to give NMR observable ammine M←NH<sub>3</sub> complexes **1a–3a**...

### 37. What Does the Revised Mechanism of the Noyori Asymmetric Hydrogenation Reaction Mean for Future Catalyst Design?

By Dub, Pavel;\* Gordon, John C.\*

For the submission to [Nature Reviews Chemistry \(2017-18\)](#), invited review (Dr. David Schilter).

